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# The use of pyrolusite to remove Pb and Cd in aqueous solutions: isotherm and thermodynamic

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**Abstract.** The utilization of natural material as an adsorbent to eliminate contaminants in the water is of great interest. Natural material can be directly used without further treatment that may lead to higher environmental impact. In this study, pyrolusite which is immensely available in Indonesia, especially in East Nusa Tenggara, was used to adsorb Cadmium (Cd) and Lead (Pb) in a single and simultaneous condition. Several operational parameters such as initial concentration, pH and temperature were applied to elaborate the sorption mechanism and to determine the adsorption capacity. The amount of absorbed Cd and Pb increased at a higher pH and reached the optimum condition at pH 7 for both. The adsorption isotherm for both adsorbates were best modeled following the Langmuir equation, giving an adsorption capacity as high as 108.70 mg/g and 123.45 mg/g for Cd and Pb respectively. Additionally, the thermodynamics data showed that the adsorption process in this study was endothermic process.

## 1. Introduction

The unexpected presence of Cd and Pb in the water system will cause serious effects on human health such as necrosis, proteinuria, gastrointestinal and neurology problem, even lead to malformation and cancer in the worst case [1-3]. Therefore, continual effort to find the most feasible technique to eliminate Cd and Pb from the contaminated water. Chemical precipitation, by adjusting the pH of the solution or after coagulation–flocculation process, is considered as the easiest method to remove heavy metals. However, this treatment produces excessive sludge that needs to be further treated [4]. Filtration, including membrane and ultra-membrane system; reverse osmosis and electro-dialysis are other systems, but less effective in term of operational and economic perspective [5,6]. Meanwhile, the application of the biological approach is still ongoing process as stability on the performance needs to be improved. Adsorption has been widely used on different scale because of its simplicity in operation and high efficiency over a wide range of concentrations [7]. Currently, there are many researches focus on the investigating and/or modifying adsorbent materials in order to find ones that have high adsorption capacity [8]. Assorted materials encompassing natural minerals (soils), industrial by-products (e.g. fly ash, steel slag), agricultural products (e.g. rice husk, sawdust, peanut shells), fishing waste (e.g. Shrimp and crab shells) have been reported to have high adsorption capacity [9]. Among those materials, natural minerals (soils) with oxides based content such as Iron and Manganese oxides

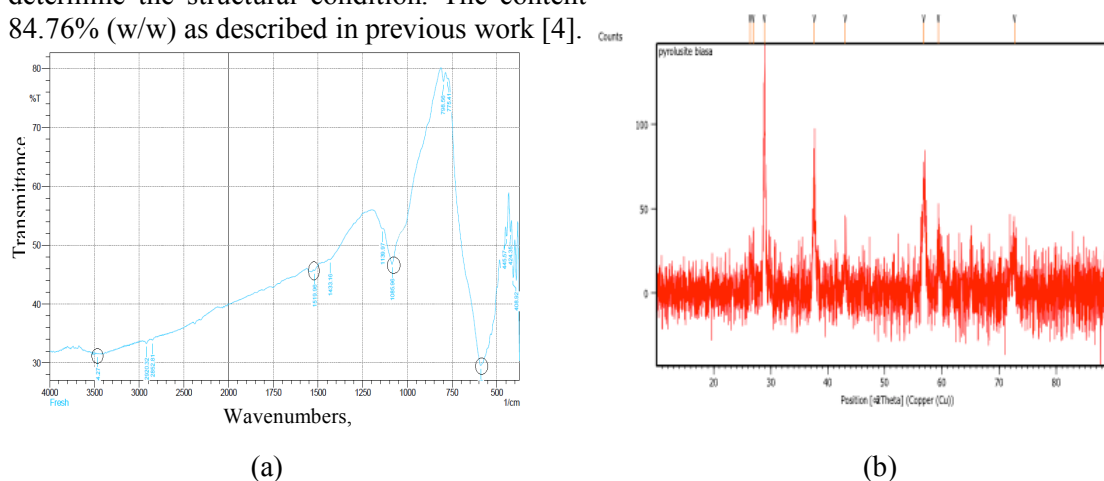


are highly preferred. Oxides based minerals usually found with a poor crystalline structure and known as a potent scavenger of trace metals in soil, sediment, and water [1]. Manganese has been known as one of the most common minerals on earth [10]. One of the most important Manganese oxide minerals is pyrolusite, which has low economical value in the natural state. Pyrolusite is massively available in Indonesia especially in East Nusa Tenggara. For this particular mineral, single chains of edge-sharing  $\text{Mn(IV)O}_6$  octahedral share corner with other chains to build a framework structure accommodating tunnels of square cross sections that are one octahedron by one octahedron [11]. Pyrolusite is an essential material used as an oxidant in organic synthesis and for industrial battery, however information on its potential function in wastewater or water treatment area is still limited. The utilization of manganese (di)oxides as an adsorbent for water contaminants have been reported by several papers. Manganese oxide in synthetic form (AMO – amorphous manganese oxide and MOF - manganese dioxide formed in situ) was used to remove Cu, Cd, Pb and Zn [7,12]. The application of beta manganese dioxide ( $\beta\text{-MnO}_2$ ) to eliminate Pb(II) in a single condition was successfully presented by considering several parameters [1]. Meanwhile the use of natural manganese dioxide to eliminate Cu in aqueous solutions had been successfully presented by Demirkiran (2015), with the efficiency as high as 96.5%. In spite of the existing information, further investigation is still needed to have a better understanding on the performance of pyrolusite as an adsorbent for heavy metals. Based on that consideration, a set of batch experiments was conducted to evaluate the mechanism of pyrolusite to adsorb Cd and Pb in aqueous solutions.

## 2. Materials and Method

### 2.1. Materials

The entire chemicals used in this study, including  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdNO}_3$ , HCl, NaOH,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  and Sodium oxalate were in analytical grade and no treatment needed prior to the utilization. Pyrolusite, an ore form of manganese dioxide was supplied by a private company in Surabaya. Characterization of pyrolusite was done by titration process to quantify the manganese oxides content, Fourier Transform Infra-red (FTIR, Shimadzu) to identify the surface functional groups and X-ray diffraction (XRD) to determine the structural condition. The content of manganese oxides in pyrolusite was as high as 84.76% (w/w) as described in previous work [4].



**Figure 1.** (a) FTIR spectra for pyrolusite; (b) XRD pattern for pyrolusite.

As described in figure 1(a), the result of FTIR analysis indicating a stretching vibration of Mn-O and Mn-O-Mn bonds at the peak of  $590\text{cm}^{-1}$ . Two other peaks, at  $1085\text{cm}^{-1}$ , expresses a vibration of hydroxyl groups that are joined to Mn atoms, and at  $1519\text{cm}^{-1}$  reveals bending vibration of O-H and  $\text{H}_2\text{O}$  which insinuates that water molecule exists in the nanostructure. In addition, the rise at peak of  $3464\text{cm}^{-1}$  indicating stretching vibration on O-H bond and bending vibration of the absorbed water molecule in the lattice. XRD analysis was conducted with Cu K $\alpha$  radiation ( $1.544\text{\AA}$ ) and operated at the voltage of 40kV and tube current of 30mA. Figure 1(b) portrays the peaks that appear

( $2\theta=28.8949^\circ$ ;  $37.6337^\circ$ ;  $43.0352^\circ$ ;  $56.8375^\circ$ ;  $59.4419^\circ$ ) are mostly reflections of manganese dioxide (except value at the peak of  $2\theta=72.6963^\circ$ ), indicating a relatively high purity of the material.

## 2.2. Method

All batch experiments in this study were conducted at temperature  $T=298\text{K}$  and under ambient conditions. To evaluate the effect of pH on the adsorption process, 200 mL of heavy metal solutions (Cd or Pb) with the initial concentration of 10 mg/L were prepared into the conical flask, follow to that, 2.5 g/L pyrolusite was added. The flask was put on thermo-shaker for mixing at 160 rpm, and at certain interval sampling was done until reaching equilibrium condition. Sample solutions were filtered using membrane filter 0.45  $\mu\text{m}$  (Sartorius) prior to analysis with UV – Spectrometer (HP series 8453). The desired pH level (4, 5, 6, 7) for both metals solutions was set using either 0.1 M HCl or NaOH. The reduction of heavy metals concentration in aqueous solutions expressed as removal efficiency that can be calculated with equation (1). The adsorption capacity ( $q_e$ ) was defined by equation (2) and also used in the determination of isotherm models.

$$\text{Removal efficiency (\%)} : R = \frac{C_0 - C_e}{C_0} * 100\% \quad (1)$$

$$\text{Adsorption capacity (} q_e, \text{ mg/g)} : q_e = \frac{(C_0 - C_e)}{m} * V \quad (2)$$

Where  $C_0$  is the initial concentration of Cd or Pb (mg/L),  $C_e$  is the concentration of heavy metals at equilibrium condition (mg/L),  $q_e$  (mg/g) is Cd or Pb adsorbed at given mass of adsorbent in the working volume (L). Adsorption isotherm models were developed by running batch experiments in different initial concentrations. The collected data of equilibrium concentrations for each metal were analyzed by using two adsorption models, Langmuir and Freundlich.

$$\text{Langmuir} : q_e = \frac{b q_{\max} C_e}{1 + b C_e} \quad (3) \quad \text{Freundlich} : q_e = k_f C_e^n \quad (4)$$

where  $C_e$  is the heavy metals concentration in the solution at equilibrium (mg/L),  $b$  is Langmuir constant related to the affinity of binding sites (L/mg),  $q_{\max}$  is the maximum adsorption capacity (mg/g),  $k_f$  is a Freundlich constant related to roughly adsorption capacity (mg/L),  $n$  is the constant related to adsorption density. In order to have an understanding on the effect of temperature, another series of batch experiments in three different temperatures (298K, 308K and 318K) were carried out. Thermodynamic data expressed as values of standard enthalpy change ( $\Delta H^\circ$ ), standard entropy change ( $\Delta S^\circ$ ) and Gibbs's free energy ( $\Delta G^\circ$ ). Those values can be determined by applying these equations:

$$K_d = \frac{C_s}{C_e} \quad (5) ; \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6) ; \quad \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

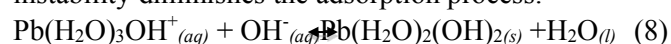
where  $C_s$  and  $C_e$  are then removed and remaining concentrations of heavy metals, respectively.  $R$  (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>) is the ideal gas constant,  $T$  is temperature in Kelvin. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were defined from the slope and y-intercept on the plot between  $\ln K_d$  versus  $1/T$ .

## 3. Results and Discussion

### 3.1. Effect of pH

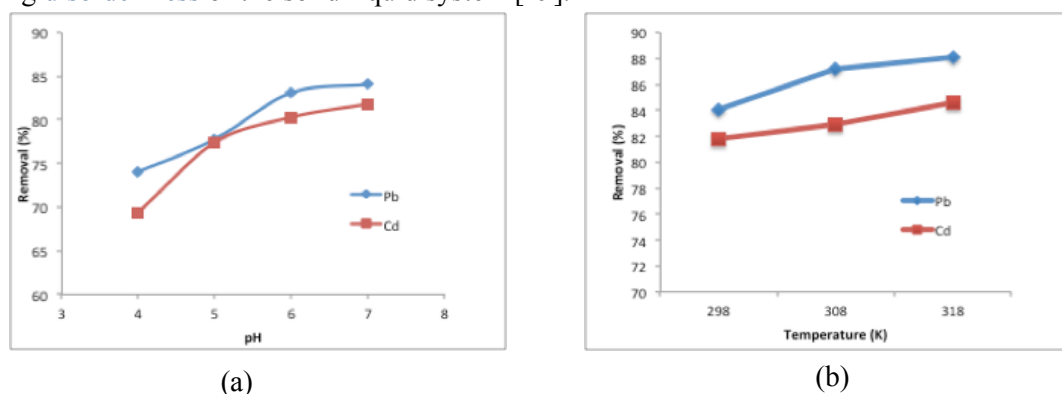
Figure 2(a) depicts the transition of Pb and Cd removal from the aqueous solutions at different pH. The trends were similar for both metals, initially steep at pH 4 to 6 then the change was relatively flat at the pH of 6 to 7. In all pH conditions, the removal of Pb was higher than Cd, with the best achievement at pH = 7 which were 84.06% and 81.82% respectively. At acid condition (pH < 7), the

main species of Pb and Cd are  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , thus the removal is mainly driven by the adsorption process. The surface charge of pyrolusite will then very crucial in determining the portion of the adsorbed metals. Several papers mentioned that pyrolusite ( $\text{MnO}_2$ ) has a net charge of zero at the pH of 1.4 to 4.5, known as  $\text{pH}_{\text{pzc}}$  (point of zero charge) [13-15]. Lately from a deeper investigation, it was confirmed that the  $\text{pH}_{\text{pzc}}$  of pyrolusite is 4.2 [1]. This means that if the pH solution is above 4.2 the surface charge of pyrolusite will tend to be negative due to the deprotonation process, in which hydrogen ions leave the sites [16]. This phenomenon causes the decreasing of electrostatic repulsion between the adsorbent and metal ions, as a consequence, the interaction will be more intense since electrostatic attraction being dominant. Minor change in the portion of metals removed at pH 6 to 7 can be explained from the speciation of Pb and Cd, at pH 6.69 – 7 for Pb and 9.03 for Cd the solubility of both metals decrease significantly and tend to precipitate (as described in reaction 8 and 9), this instability diminishes the adsorption process.



### 3.2. Effect of Temperature

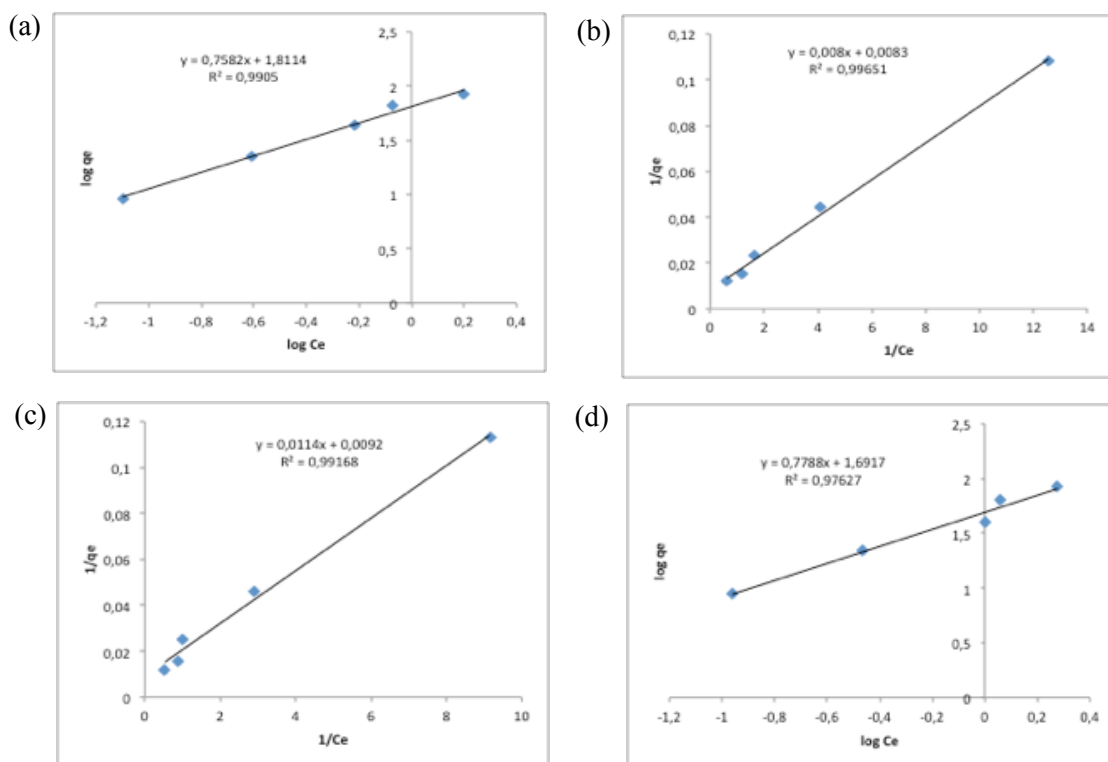
The removal of Pb and Cd through the adsorption process in three different temperatures is presented in figure 2(b). For both metals, the highest removal was achieved at 318K which were 88.07% and 84.60% for Pb and Cd respectively. The results indicate that the adsorption process of Pb and Cd onto pyrolusite was more favorable at higher temperature. A plausible elucidation for this is that dissolved metals need to destroy the hydration sheaths prior to the adsorption process. The destruction process needs energy, while the adsorption process of metals onto pyrolusite emits energy. The need for energy seems to be more than the available source, thus in higher temperature, the elimination of heavy metal ions is more effective. Adsorption mechanism of Pb and Cd on pyrolusite can be evaluated from thermodynamic data, as provided in Table I. The positive value of standard enthalpy ( $\Delta H^\circ$ ) relates to the information that the adsorption process is endothermic. The low value of  $\Delta H^\circ$  in this experiment is similar to that found in [1], confirming that the adsorption process of Pb onto pyrolusite is weak, which also applies for Cd. However, since the value of  $\Delta H^\circ$  for both metals is still bigger than 4200 J/mol, the weak adsorption process is still determined by chemical reaction [17]. The negative value of  $\Delta G^\circ$  reflects the spontaneous process, at a higher temperature the process is more spontant. The lower  $\Delta G^\circ$  value the lesser energy required for the attachment process of adsorbent – adsorbate [18]. In this case, the need of energy for adsorption process of Pb to pyrolusite is smaller compared to Cd. The positive value of  $\Delta S^\circ$  suggests structural changes in adsorbate and adsorbent creating disorder-ness of the solid-liquid system [19].



**Figure 2.** (a) Removal of Pb and Cd in different pH value; (b) Removal of Pb and Cd in different temperature

**Table 1.** Thermodynamic data of the adsorption of Pb and Cd

T (K)	C <sub>0</sub> (mg/L)	$\Delta S^0$ (J/mol.K)	$\Delta H^0$ (J/mol)	$\Delta G^0$ (J/mol)
<b>Pb</b>				
298	10	72.18	13335.66	-8173.98
308	10	72.18	13335.66	-8895.78
318	10	72.18	13335.66	-9617.58
<b>Cd</b>				
298	10	52.15	7851.74	-7688.96
308	10	52.15	7851.74	-8210.46
318	10	52.15	7851.74	-8731.96

**Figure 3.** (a) Linear plot of Langmuir for Pb, (b) Linear plot of Freundlich for Pb, (c) Linear plot of Langmuir for Cd and (d) Linear plot of Freundlich for Cd**Table 2.** Langmuir and Freundlich isotherm parameters for Pb and Cd

Model	Parameter	Pb	Cd
Langmuir	b (L/mg)	1.01	0.88
	q <sub>max</sub> (mg/g)	123.45	108.70
Freundlich	K <sub>f</sub> (mg/g)	64.71	49.09
	n	0.76	0.78

### 3.3. Adsorption Isotherms

In this study, Langmuir and Freundlich were applied to identify the **isotherms adsorption** that can be used to describe the distribution of adsorbate in the liquid and solid phases. The collected data of each metal concentration at equilibrium condition ( $C_e$ ) were plotted versus the amount of adsorbed metal in pyrolusite ( $q_e$ ) following the equation (3) and (4) for Langmuir and Freundlich model respectively.

The result of the analysis provides information that for both metals, Langmuir model fits better than Freundlich model to elaborate adsorption process onto pyrolusite (Figure 3), which is expressed by the higher value of  $R^2$  (0.99651 and 0.99168 – Langmuir for Pb and Cd respectively compared to 0.99050 and 0.97627 – Freundlich for Pb and Cd). Langmuir model suggests that the adsorption mechanism is driven by the chemical process (chemisorption) through three stages, which are external diffusion, internal diffusion and chemical interaction. The finding that the Langmuir model is more suitable to the adsorption data also indicates that pyrolusite has a homogenous surface and as the result of creating identical adsorption activity. Pb and Cd are adsorbed by forming a complete monolayer all around the surface of adsorbate. By that, the assumption of interaction between adsorbate following the formation of monolayer as suggested by the Freundlich model is negligible. Following to that, the maximum adsorption capacity of pyrolusite for Pb and Cd determined by the preferred model was 123.45 mg/g and 108.70 mg/g respectively. The adsorption capacity of pyrolusite, a natural manganese dioxide, for Pb and Cd is superior if compared to other natural materials. For example, by using kaolin, fly ash, blast furnace slag and bentonite, it was reported the adsorption capacity (mg/g) for Pb were 4.50; 5.00; 5.50 and 7.60 respectively [20]. The use of Australian zeolite could reduce Pb and Cd as much as 9.97 mg/g and 6.72 mg/g, comparable to that the Korean zeolite that had the adsorption capacity of 8.90 mg/g and 7.10 mg/g respectively [11, 21]. Considering the finding, pyrolusite could be used as an effective and low cost adsorbent for heavy metals.

#### 4. Conclusions

Pyrolusite was successfully tested as an alternative adsorbent for Cd and Pb in aqueous solutions. The thermodynamic data and isotherm model that the adsorption process for both metals is endothermic and spontaneous, indicating that chemical reaction drove the mechanism. The adsorption capacity of pyrolusite for Cd and Pb following the Langmuir model were 108.70 mg/g and 123.45 mg/g respectively.

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